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(73) Proprietor: **NIPPON OIL AND FATS COMPANY, LIMITED**
10-1, Yuraku-cho 1-chome
Chiyoda-ku
Tokyo 100 (JP)

(72) Inventor: **Ohama, Yoshifumi**
6-11, Mondo Okada-cho
Nishinomiya-shi
Hyogo (JP)
Inventor: **Chihara, Yoshihide**
1-15-16, Nanpeidai
Takatsuki-shi
Osaka (JP)
Inventor: **Honda, Yasufumi**
6-23, Mondo Odaka-cho
Nishinomiya-shi
Hyogo (JP)
Inventor: **Miyamoto, Yasuhiro**
6-23, Mondo Odaka-cho
Nishinomiya-shi
Hyogo (JP)

(74) Representative: **Hansen, Bernd, Dr.rer.nat. et al**
Hoffmann, Eitle & Partner
Patentanwälte
Postfach 81 04 20
D-81904 München (DE)

Description

This invention relates to a ultraviolet-curable coating composition which can be coated in large film thickness in one operation and be cured sufficiently even with insufficient ultraviolet irradiation to form a cured film excellent in appearance (distinctness of image gloss), adhesion and weathering resistance.

Solvent type or water-soluble type acrylic/melamine resin coatings and acrylic/urethane resin coatings have widely been employed as coatings for vehicle bodies which are required to have a highly attractive appearance as well as other various coating performances. In recent years, photo-curable coatings and radiation-curable coatings have been proposed in addition to the above-described coatings curable by crosslinking. The photo-curing coatings include a composition comprising a modified isocyanate having an ethylenical double bond and an isocyanate group and a hydroxyl-containing prepolymer as disclosed in Japanese Patent Application (OPI) No. 66596/75 (the term "OPI" as used herein means "unexamined published application"). The radiation-curable coatings include a composition comprising an ethylenic polymer having a (meth)acrylic ester and a hydroxyl group, a vinyl polymer, and a photo initiator as basic components and, in addition, a reaction product between the basic components and a polyisocyanate compound as disclosed in Japanese Patent Application (OPI) No. 17967/79.

The aforesaid acrylic/melamine resin coatings and acrylic/urethane resin coatings do not necessarily exhibit satisfactory appearance and are difficult to be coated in a high film thickness. A high film thickness may be attained by increasing the non-volatile residue, i.e., total solids, of the coating. However, means generally taken to this effect, such as reduction of molecular weight of resinous components to decrease the viscosity, result in deterioration of workability of the coating and physical properties, chemical resistance, and weathering resistance of a coating film.

On the other hand, the photo-curable coatings or radiation-curable coatings are easily obtained in a high film thickness and their coating films are excxellent in appearance. However, they show poor adhesion to a substrate due to great distortion upon curing. Moreover, sufficient curing cannot be achieved on areas where ultraviolet radiation is insufficient so that satisfactory weathering resistance cannot be always assured.

JP-A-59 130 568 (referred to in Chemical Abstract 102,47052d, 1985) relates to UV curable coating compositions comprising (A) tetraethylene glycol dimethacrylate, (B) OH-containing methacrylate copolymer, (C) TDI-TMP prepolymer, benzophenone and hydrochinone. This mixture provides a protective acrylic coating with good adhesion and hardness.

GB-A-2 109 385 discloses a two-coat, one-bake metallic coating method which comprises applying, first, (a) a base coat composition containing an acrylic polyol oligomer having an average molecular weight of 500 to 2000 and a non-yellowing polyisocyanate compound in a NCO/OH ratio of 0.5/1 through 1/1.5 and further containing an appropriate amount of a metallic pigment and, then, on top thereof (b) a clear top coat composition containing said acrylic polyol oligomer and a non-yellowing polyisocyanate compound in a NCO/OH ratio of 0.5/1 through 1/0.5 and causing the resulting coats to cure simultaneously.

According to EP-A-407 a substrate is treated with a radiation curable coating composition based on a polyester resin esterified with acrylic acid and/or methacrylic acid, a vinyl compound and a photoinitiator, the coating composition being dried under the influence of ultraviolet light having a wave length of 200 to 600 nm. The polyester resin has a hydoxyl number of 50 to 250 and an ethylenic unsaturation equivalent weight in the range of 200 to 10,000 g., and the composition also contains a polyisocyanate in an amount of 0.7 to 1.3 equivalents, pref. 0.9 to 1.1 equivalents, of isocyanate per equivalent of hydroxyl contained in the composition,

The coating may be applied, for instance, as automobile paint.

It is, an object of this invention is to provide a ultraviolet-curable coating composition with which one can obtain a high film thickness in one coating and which can be cured sufficiently even when ultraviolet irradiation is non-uniform, and provide high quality coating films excellent in appearance, adhesion to a substrate and weathering resistance.

As a result of extensive investigations to accomplish the above object, it has now been found that a composition comprising a specific ultraviolet-curable polyfunctional (meth)acrylate, a specific urethane-curing polymer, and a specific polyisocyanate compound in a specific compounding ratio and having incorporated therein a photo stabilizer and a photopolymerization initiator provides a coating film of high thickness in one coating and is sufficiently cured even with non-uniform ultraviolet radiation and that the coating film obtained from such a composition fully satisfies various requirements, such as appearance, adhesion and weathering resistance. The present invention has been completed based on these findings.

The present invention relates to an ultraviolet-curable coating composition for vehicle bodies comprising:

(A) 30 to 70 % by weight based on the total amount of (A), (B) and (C) of an ultraviolet-curable polyfunctional (meth)acrylate containing at least two (meth)acryloyl groups in the molecule thereof and having a number average molecular weight of from 190 to 2,000;

(B) a polyhydric alcohol mono(meth)acrylate polymer having a hydroxyl number of from 10 to 200 selected from homopolymers of hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, neopentyl glycol mono(meth)-acrylate and glycerin mono(meth)acrylate, or copolymers comprising these monomers and one or more of other monomers copolymerizable therewith, selected from methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and styrene;

(C) a non-yellowing polyisocyanate compound having an isocyanate equivalent of from 0.4 to 1.2 per hydroxyl equivalent of component (B) selected from homopolymers of hexamethylene diisocyanate, homopolymers of isophorone diisocyanate, copolymers of hexamethylene diisocyanate with isophorone diisocyanate, mixtures thereof and blocked isocyanate compounds thereof; the total of (B) and (C) being 70 to 30 % by weight based on the total of (A), (B) and (C);

(D) a photo stabilizer from the group consisting of a hindered amine type antioxidant and a benzotriazole type ultraviolet absorbent; and

(E) a photopolymerization initiator, said composition providing a cured film having a gloss retention of 90% or more and a color difference ΔE of 2 or less when tested with a sunshine weatherometer for an exposure time of 1,000 hours.

The invention comprises also a process for preparing said ultra-violet curable coating composition comprising uniformly mixing the before-mentioned components (A) to (E) wherein component (C) has an isocyanate equivalent of from 0.4 to 1.2 per hydroxyl group equivalent of component (B), in such an amount that in the final product (A) constitutes from 30 to 70% by weight and components (B) and (C) constitute from 70 to 30% by weight of the total amount of (A), (B), and (C).

The term "(meth)acryloyl group" as used herein means an acryloyl group and/or a methacryloyl group represented by formula

$$CH_2=\underset{\underset{R}{|}}{C}-\underset{\underset{O}{\|}}{C}-$$

wherein R represents a hydrogen atom or a methyl group.

The polyfunctional (meth)acrylate which can be used as component (A) in the present invention is a ultraviolet-curable compound having at least two (meth)acryloyl groups in the molecule and a number average molecular weight of from 190 to 2,000. If the number of a (meth)acryloyl group per molecule is less than 2, curing properties of the resulting composition becomes insufficient. If the number average molecular weight exceeds 2,000, neither improvement in appearance nor assurance of curing properties can be attaiend. If it is less than 190, the resulting coating film exhibits poor flexibility.

The polyfunctional (meth)acrylate to be used in the present invention includes not only polyhydric esters between polyhydric alcohols and acrylic acid and/or methacrylic acid (hereinafter inclusively referred to as (meth)acrylic acid) but various (meth)acrylate compounds hereinafter described. These polyfunctional (meth)acrylates can be used either individually or in combinations of two or more thereof.

Specific examples of the aforesaid polyhydric esters are 1,3-butanediol di(meth)acrylate, diethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, hydroxypivalic ester neopentyl glycol di(meth)-acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate and dipentaerythritol hexa-(meth)acrylate.

Examples of (meth)acrylate compounds other than the above-enumerated polyhydric esters include polyester acrylates composed of n mols of adipic acid, (n+1) mols of hexanediol, and 2 mols of (meth)-acrylic acid; epoxy (meth)acrylates obtained by esterifying an epoxy group of an alicyclic epoxy compound with (meth)acrylic acid; polyurethane (meth)acrylates obtained by reacting hexamethylene diisocyanate with a (meth)acrylate having a hydroxyl group, e.g., hydroxyethyl acrylate; melamine (meth)acrylate obtained by reacting a methylol group of methylolmelamine with hydroxyethyl (meth)acrylate.

Of these polyfunctional (meth)acrylates, those containing an acryloyl group in their molecule are particularly preferred because they bring more satisfactory results in curing properties as compared with those containing a methacryloyl group. It is most preferred to use a polyfunctional acrylate containing 3 or more acryloyl groups in the molecule either alone or in combination with a polyfunctional acrylate

containing two acryloyl groups in the molecule.

The polyhydric alcohol mono(meth)acrylate polymer which can be used as the component (B) includes homopolymers or copolymers of hydroxyl-containing monomers, e.g., hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate and glycerin mono(meth)acrylate, or copolymers comprising these monomers and one or more of other monomers copolymerizable therewith, e.g., methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and styrene.

Preferred of these polymers are copolymers comprising 2-hydroxyethyl (meth)acrylate and/or 2-hydroxypropyl (meth)acrylate as a hydroxyl-containing monomer and the aforesaid copolymerizable monomer(s).

The hydroxyl number of the component (B) is limited to a range of from 10 to 200. If it is less than 10, curing properties are not satisfied in some cases. If it exceeds 200, there is a fear that various performance properties, such as coating film appearance, adhesion, and weathering resistance, may be impaired.

The molecular weight of the component (B) is not particularly limited but usually ranges from about 2,000 to about 20,000.

The non-yellowing polyisocyanate compound which can be used as the component (C) includes polymers of hexamethylene diisocyanate and/or isophorone diisocyanate, that is, a homopolymer of hexamethylene diisocyanate, a homopolymer of isophorone diisocyanate, a copolymer of hexamethylene diisocyanate and isophorone diisocyanate, and a mixture thereof. Blocked isocyanate compounds of these polymers wherein the isocyanate group is masked with a hydroxyl-containing compound are preferred.

The components (A), (B), and (C) are present in such proportions that the component (A) be present in an amount of from 30 to 70% by weight, based on the total amount of these three components and the components (B) and (C) are present in an amount of from 70 to 30% by weight, based on the total amount of the three components, with the isocyanate equivalent in the component (C) ranging from 0.4 to 1.2, per hydroxyl equivalent in the component (B).

The photo stabilizer as component (D) functions to improve weathering resistance of a coating film. It is selected from compounds which can be uniformly dissolved or dispersed in a coating film and causes neither inhibition of ultraviolet-curing nor yellowing of a coating film. Such compounds are hindered amine type anti-oxidants and benzotriazole type ultraviolet absorbents. These photo stabilizers are usually used in an amount of from about 0.5 to about 5 parts by weight per 100 parts by weight of the total amount of the components (A), (B), and (C).

The photopolymerization initiator which can be used as component (E) shows absorption in the ultraviolet region of from 260 to 450 nm and includes for example benzoin, derivatives of benzophenone and, acetophenone, Michler's ketone, tetraalkylthiuram monosulfides and thioxanes. Preferred among them are acetophenone and its derivatives. These photopolymerization initiators may be used either individually or in combinations of two or more thereof. The amount of the component (E) to be added usually ranges from about 0.5 to 5 parts by weight per 100 parts by weight of the total amount of the components (A), (B), and (C).

The ultraviolet-curable coating composition according to the present invention can be prepared by uniformly mixing the above-described components (A) to (E). In the preparation, a diluting solvent may be used for viscosity control in such an amount that total solids may not be less than about 40% by weight. If desired, the composition may further contain additives generally employed in ultraviolet-curable coatings, such as photopolymerization sensitizers, e.g., amine compounds, urea compounds, sulfur compounds, etc.; anti-cissing agents, fluidity-controlling agents, organic peroxides for effecting uniform curing on polymerization, pigments and dyes.

The ultraviolet-curable coating composition according to the present invention provides a cured film having very excellent weathering characteristics, such as a gloss retention of 90% or more and a color difference ΔE of 2 or less when tested with a sunshine weatherometer for an exposure time of 1,000 hours. Such superiority can first be achieved by an appropriate combination of the essential components (A) to (E), particularly, in a specific proportion of each components (A), (B) and (C) as described above but has not been substantially attained by any of the conventionally known ultraviolet-curable coatings.

The method of coating the ultraviolet-curable coating composition of the present invention is not particularly restricted. In general, a substrate is previously coated with a baking-curable colored coating. After baking, the composition of the present invention is spray-coated or electrostatically coated thereon with, if necessary, a marking tape, etc. adhered thereto. The coating film is then cured by irradiation with ultraviolet rays. If desired, the coating film may be pre-heated to remove the solvent prior to ultraviolet light irradiation, or the ultraviolet light irradiation may be followed by post-heating.

A ultraviolet light emitter to be used for curing is preferably capable of irradiating a surface of three-dimensional substrate as uniformly as possible. The ultraviolet light source to be used includes a high-pressure mercury lamp and a metal halide lamp.

The polyfunctional (meth)acrylate as component (A) contributes to improve ultraviolet-curable properties and to reduce a requisite amount of a diluting solvent, which leads to realization of a large coating thickness in one coating operation. Further, the component (A) covers up roughness of a substrate surface to produce high quality appearance..

The polyhydric alcohol mono(meth)acrylate as component (B) and the non-yellowing polyisocyanate compound as component (C) play an important role in compensation for insufficiency of curing when ultraviolet irradiation is non-uniform. They are also effective to greatly reduce distorsion due to shrinkage on curing thereby to improve adhesion to a substrate and weathering resistance and, at the same time, to make a satisfactory finish on the areas where the coating is applied on a marking tape without suffering from defects, such as wrinkles and cracks.

In the present invention, the crosslinking density of a coating film can be controlled appropriately by varying the mixing ratio of the components (A), (B), and (C), to obtain performance properties in accordance with use of the coating composition, such as resistance to gasoline and wearability.

The photo stabilizer as component (D) improves the weathering resistance of a cured film. Of the photo stabilizers, ultraviolet absorbents have generally been regarded unfavorable for use in ultraviolet-curable compositions in view of their curing properties. Nevertheless, use of such ultraviolet absorbents in the coating composition of the present invention do not prevent the curing of a coating film.

The ultraviolet-curable coating composition comprising the components (A) to (D) having the above-described effects and, in addition, a photopolymerization initiator as component (E) can be coated in large thickness in one coating operation and can be sufficiently cured even when ultraviolet irradiation is non-uniform, and provides a cured coating film having excellent performances, such as appearance, adhesion and weathering resistance. Therefore, it is very useful as a coating for vehicle bodies (steel plates or plastics) which is especially required to satisfy appearance and weathering characteristics as well as a coating for other substrates, e.g., a metal plate other than a steel plate, and wooden products.

The present invention will now be illustrated in greater detail by way of the following examples, but it should be understood that the present invention is not deemed to be limited thereto. In these examples, all parts and percents are given by weight unless otherwise indicated.

EXAMPLES 1 TO 5

Components (A) to (E) shown in Table 1 were uniformly mixed to prepare a ultraviolet-curing coating composition (clear coating).

COMPARATIVE EXAMPLES 1 TO 3

Components (A) to (E) shown in Table 1 were uniformly mixed to prepare a comparative ultraviolet-curable coating composition (clear coating).

COMPARATIVE EXAMPLE 4

A water-soluble acrylic melamine resin clear coating ("Aqua No. 7100 Clear" produced by Nippon Oils & Fats Co., Ltd.; total solids: 40%) was used as a comparative coating.

TABLE 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1	Comparative Example 2	Comparative Example 3
Component (A):(part):								
A_1 *1)	53	31.5	47	-	-	91.6	-	-
A_2 *2)	-	-	-	20.5	62.5	-	5.1	33.4
A_3 *3)	-	12.3	-	-	-	-	-	-
A_4 *4)	-	-	-	11.4	-	-	-	13.3
Component (B):(part):								
B_1 *5)	42	50	-	-	-	7.4	-	-
B_2 *6)	-	-	37	39.9	31.3	-	81.6	46.7
Component (C):(part):								
C_1 *7)	5	6.2	16	-	-	1	13.3	-
C_2 *8)	-	-	-	20.2	6.8	-	-	6.6
Component (D):(part**):								
D_1 *9)	1	1.2	1	-	-	-	-	-
D_2 *10)	-	-	1	1.2	1.2	1	1	-
Component (E):(part**):								
E_1 *11)	1	1.2	1	-	-	2	1	-
E_2 *12)	-	-	-	1.3	1.2	-	-	1.3

/to be cont'd.

TABLE 1 (cont'd.)

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1	Comparative Example 2	Comparative Example 3
Solid Weight Ratio of (A)/(B)+(C)	51/49	46/54	44/56	44/56	64/36	91/9	5/95	50/50
Equivalent Ratio of NCO in (C)/OH in (B)	0.62	0.64	1.20	1.00	0.40	0.68	0.46	0.27
Total Solids (wt%)	64	69	66	73	71	62	70	75

Note: **: Part by weight per 100 parts by weight of (A)+(B)+(C).

*1) A_1: A solution (total solids: 63%) of polyurethane acrylate having a number average molecular weight of 1,800, which is obtained by reacting 1,008 parts of Coronate® HK50EX (a polymer of hexamethylene diisocyanate produced by Nippon Polyurethane Ind. Co., Ltd.; isocyanate group content: 10.2%), 348 parts of 2-hydroxypropyl acrylate, 0.2 part of hydroquinone, and 0.1 part of triethylamine at 80°C for 10 hours.

*2) A_2: A solution (total solids: 75%) of epoxy acrylate having a number average molecular weight of 800, which is obtained by reacting 450 parts of Araldite® XB-3084 (hydrogenated epoxy resin produced by Ciba Ltd.; epoxy equivalent: 227), 144 parts of acrylic acid, 0.2 part of hydroquinone, 2 parts of triethylamine, and 200 parts of xylene at 150°C for 5 hours.

*3) A_3: Trimethylolpropane triacrylate (number average molecular weight: 300)

*4) A_4: Polyethylene glycol (400) diacrylate ("PEG 400DA" produced by Nippon Oils & Fats Co., Ltd.; number average molecular weight: 520)

*5) B_1: A solution (total solids: 67%) of a polymer

having a hydroxyl number of 65, which is obtained by mixing 13 parts of 2-ethylhexyl acrylate successively with 50 parts of butyl methacrylate, 15 parts of 2-hydroxyethyl methacrylate, 2 parts of methacrylic acid, 20 parts of styrene, 2 parts of azobisisobutyronitrile, and 48 parts of toluene and allowing the mixture to react at 110°C for 6 hours while stirring.

*6) B_2: A solution (total solids: 70%) of a polmer having a hydroxyl number of 113, which is obtained in the same manner as for B_1, except for using double the amount of 2-hydroxyethyl methacrylate.

*7) C_1: A polymer of hexamethylene diisocyanate ("Sumidur® N" produced by Sumitomo Bayer Urethane Co., Ltd.)

*8) C_2: A polymer of isophorone diisocyanate ("Desmodur® Z4370" produced by Sumitomo Bayer Urethane Co., Ltd.)

*9) D_1: Hindered amine type antioxidant ("Sanol® LS-292" produced by Sankyo Co., Ltd.)

*10) D_2: Benzotriazole type ultraviolet absorbent ("Tinuvin® 900" produced by Ciba Ltd.)

*11) E_1: Acetophenone type photopolymerization

initiator ("Irgacure® 184" produced by Chiba Ltd.)

*12) E_2: Acetophenone type photopolymerization initiator ("Darocur® 1173" produced by Merck AG)

Test specimens were prepared as follows using each of the coatings of Examples 1 to 5 and Comparative Examples 1 to 4 and were evaluated for coating performances according to the test methods described below. The results of evaluation are shown in Table 2.

Preparation of Specimens:

A fuel tank of 17 ℓ in volume for use in an autocycle having 498 cc in total exhaustion (hereinafter referred to as substrate A) or a steel plate SPCC-SB measuring 70 mm in length, 150 mm in width, and 1 mm in thickness (hereinafter referred to as substrate B) was treated with zinc phosphate and then electrostatically coated with a water-soluble acrylic resin coating ("Aqua No. 7100 Balck" produced by Nippon Oils & Fats Co., Ltd.) to a dry thickness of 30 µm, followed by heating at 150 °C for 30 minutes.

On the acrylic resin-coated substrate was further applied each of the coatings of Examples and Comparative Examples to a prescribed dry thickness by spray-coating or electrostatic coating with or without a marking tape (produced by Sumitomo 3M Co., Ltd.) being adhered on the acrylic resin film, followed by setting at room temperature for 10 minutes.

Each of the substrates coated with the coatings of Examples 1 and 3 to 5 and Comparative Examples 1 to 3 was heated with a far infrared heater ("Infrastein®" produced by Nippon Gaishi Co., Ltd.) at uniformly irradiated with ultraviolet light for 2 seconds using a high-pressure mercury lamp ("Hi-Cure Lamp" manufactured by Nihon Denchi Co., Ltd.; length: 20 cm; 3 bulbs total of 4.8 kW) placed at a distance of about 20 cm from the substrate. After ultraviolet irradiation, the substate was further heated with a far infrared heater at a substrate temperature of 120 °C for 5 minutes.

The substrate coated with the coating of Example 2 was treated in the same manner as above, except that ultraviolet light irradiation was carried out for 3 seconds using a metal halide lamp (manufactured by Nihon Denchi Co., Ltd.; length: 20 cm; 3 bulbs each of 3.8 kW) as a ultraviolet light source.

The substrate coated with the coating of Comparative Example 4 was heated with a far infrared heater at a substrate temperature of 150 °C for 30 minutes.

Evaluation of Performance Properties:

Maximum Film Thickness

The coating was applied on substrate B by spray-coating or electrostatic coating with no marking tape. The maximum thickness of a normal coating film formed in one coating operation was measured. The term "normal" for the coating film means that the film is free from any abnormality, such as sags, runs, and foaming, either during coating or during curing. A maximum thickness of 60 µm or more was taken as an acceptances criterion.

Gloss Retention

Substrate B onto which a marking tape had been adhered was electrostatically coated with the coating to a dry thickness of 70 µm in Examples 1 to 5 and Comparative Examples 1 to 3 or 40 µm in Comparative Example 4. The test specimen (cured) was subjected to weathering test using a sunshine weatherometer according to JIS K5400, and a gloss retention after a weatherometer exposure time of 1,000 hours (a percent retention based on the initial gloss) was determined.

Color Difference (ΔE)

Weathering test was carried out on the same specimens in the same manner as for evaluation of gloss retention according to JIS D0202. The color difference ΔE after a sunshine weatherometer exposure time of 1,000 hours was calculated from equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

wherein

$$\Delta L = (L_1 - L_2);$$
$$\Delta a = (a_1 - a_2);$$
$$\Delta b = (b_1 - b_2);$$

L_1, a_1, and b_1 each represents an initial value; and
L_2, a_2, and b_2 each represents a value after testing.

Distinction of Image Glass

Appearance of the same specimens as used for evaluation of gloss retention was evaluated for distinctness of image gloss by means of a portable glossmeter (PGD-IV manufactured by Tokyo Koden K.K.). Gloss of 0.9 or higher was taken as an acceptance criterion.

Adhesion

The same specimens as used for evaluation of gloss retention were subjected to adhesion test in accordance with JIS K5400 6.15. Adhesion of 100 was rated as "good".

Coating Property on Tape

Substrate A or B on which a marking tape had been adhered was electrostatically coated with the coaing to a dry thickness of 70 µm in Examples 1 to 5 and Comparative Examples 1 to 3 or 40 µm in Comparative Example 4. The coating film on the area where the marking tape had been adhered was visually observed. A coating film suffering from no abnormality, such as cracks and wrinkles, was rated as "good".

Weathering Resistance

The same test specimens as used for evaluation of coating properties on tape were fixed to a mount at an incline of 30 degrees from the horizon and exposed to weather on the shore of Okinawa for 2 years. The coating film free from any abnormality, such as color change and cracks, and remarkable reduction of gloss was rated as "good".

TABLE 2

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Maximum Thickness (μm)	80	85	80	80	75	80	50	80	40
Gloss Retention (%)	97	98	98	93	92	43	92	76	97
Color Difference ΔE	1.2	1.1	0.8	1.2	1.4	7.2	0.9	4.5	1.2
Distinctness of Image Gloss	1.2	1.0	1.0	1.1	1.0	1.0	0.5	1.1	0.4
Adhesion	100	100	100	100	100	0	100	100	100
Coating Property on Tape:									
Substrate A	good	good	good	good	good	poor	good	good	good
Substrate B	good	good	good	good	good	poor	good	good	good
Weathering Resistance:									
Substrate A	good	good	good	good	good	poor	good	poor	good
Substrate B	good	good	good	good	good	poor	good	poor	good

It can be seen from the results of Table 2 that the ultraviolet-curable coating compositions according to the present invention exhibit excellent performance properties. Whereas, the water-soluble acrlic/melamine resin clear coating of Comparative Example 4 failed to satisfy requirements of distinctness of image gloss and maximum film thickness. The coating film of Comparative Example 1 in which the proportion of the component (B) is less than the lower limit of the present invention shows poor adhesion to a substrate, has

cracks when formed on a marking tape, and undergoes overall cracking when exposed to weather for 1 year. The coating film of Comparative Example 2 in which the proportion of the component (A) is less than the lower limit of the present invention is unsatisfactory in distinctness of image gloss and maximum film thickness. The coating composition of Comparative Example 3 which does not contain the component (D) of the present invention undergoes cracking on the entire film surface when exposed to weather for 1 year.

Claims

1. An ultraviolet-curable coating composition for vehicle bodies comprising:
(A) 30 to 70 % by weight based on the total amount of (A), (B) and (C) of an ultraviolet-curable polyfunctional (meth)acrylate containing at least two (meth)acryloyl groups in the molecule thereof and having a number average molecular weight of from 190 to 2,000;
(B) a polyhydric alcohol mono(meth)acrylate polymer having a hydroxyl number of from 10 to 200 selected from homopolymers of hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, neopentyl glycol mono-(meth)acrylate and glycerin mono(meth)acrylate, or copolymers comprising these monomers and one or more of other monomers copolymerizable therewith, selected from methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and styrene;
(C) a non-yellowing polyisocyanate compound having an isocyanate equivalent of from 0.4 to 1.2 perhydroxyl equivalent of component (B) selected from homopolymers of hexamethylene diisocyanate, homopolymers of isophorone diisocyanate, copolymers of hexamethylene diisocyanate with isophorone diisocyanate, mixtures thereof and blocked isocyanate compounds thereof; the total of (B) and (C) being 70 to 30 % by weight based on the total of (A), (B) and (C);
(D) a photo stabilizer from the group consisting of a hindered amine type antioxidant and a benzotriazole type ultraviolet absorbent; and
(E) a photopolymerization initiator, said composition providing a cured film having a gloss retention of 90% or more and a color difference ΔE of 2 or less when tested with a sunshine weatherometer for an exposure time of 1,000 hours.

2. An ultraviolet-curable coating composition as in claim 1, wherein the component (A) contains a polyfunctional acrylate having at least three acryloyl groups in the molecule thereof.

3. An ultraviolet-curable coating composition as in claim 2, wherein the component (A) further contains a polyfunctional acrylate having two acryloyl groups in the molecule thereof.

4. An ultraviolet-curable coating composition as in claim 1, wherein the component (D) is present in an amount of from 0.5 to 5 parts by weight per 100 parts by weight of the total amount of the components (A), (B), and (C).

5. An ultraviolet-curable coating composition as in claim 1, wherein the component (E) is selected from acetophenone and derivatives thereof.

6. An ultraviolet-curable coating composition as in claim 1, wherein the component (E) is present in an amount of from 0.5 to 5 parts by weight per 100 parts by weight of the total amount of the components (A), (B), and (C).

7. Process for preparing an ultraviolet-curable coating composition according to claim 1 which comprises uniformly mixing components (A) to (E) of claim 1, wherein component (C) has an isocyanate equivalent of from 0.4 to 1.2 per hydroxyl group equivalent of component (B), in such an amount that in the final product (A) constitutes from 30 to 70% by weight and components (B) and (C) constitute from 70 to 30% by weight of the total amount of (A), (B), and (C).

Patentansprüche

1. Ultravioletthärtbare Überzugszusammensetzung für Fahrzeugkörper, umfassend:
(A) 30 bis 70 Gew.-%, bezogen auf die Gesamtmenge von (A), (B) und (C) eines ultraviolett-härtbaren polyfunktionellen (Meth)acrylats, enthaltend wenigstens zwei (Meth)acryloylgruppen im

Molekül und mit einem Zahlendurchschnittsmolekulargewicht von 190 bis 2.000;

(B) ein Mono(meth)acrylatpolymer eines mehrwertigen Alkohols mit einer Hydroxylzahl von 10 bis 200, ausgewählt aus Homopolymeren von Hydroxyethyl(meth)acrylat, Hydroxypropyl(meth)acrylat, Polyethylenglykolmono(meth)acrylat, Polypropylenglykolmono(meth)acrylat, Neopentylglykolmono-(meth)acrylat und Glycerinmono(meth)acrylat oder Copolymere, umfassend diese Monomere mit einem oder mehreren anderen Monomeren, die damit copolymerisierbar sind, ausgewählt aus Methyl(meth)acrylat, Ethyl(meth)acrylat, Propyl(meth)acrylat, Butyl(meth)acrylat, 2-Ethylhexyl(meth)-acrylat und Styrol;

(C) eine nichtvergilbende Polyisocyanatverbindung mit einem Isocyanatäquivalent von 0,4 bis 1,2 pro Hydroxyäquivalent der Komponente (B), ausgewählt aus Homopolymeren von Hexamethylendiisocyanat, Homopolymeren von Isophorondiisocyanat, Copolymeren von Hexamethylendiisocyanat mit Isophorondiisocyanat, Mischungen davon und geblockten Isocyanatverbindungen davon; wobei die Gesamtmenge von (B) und (C) 70 bis 30 Gew.-%, bezogen auf die Gesamtmenge von (A), (B) und (C) beträgt;

(D) einen Fotostabilisator aus der Gruppe, bestehend aus einem Antioxidans vom gehinderten Amintyp und einem Ultraviolett-Absorbenz vom Benzotriazoltyp, und

(E) einen Fotopolymerisationsinitiator, wobei die Zusammensetzung einen gehärteten Film ergibt mit einer Glanzbeständigkeit von 90 % oder mehr und einer Farbdifferenz ΔE von 2 oder weniger, getestet mit einer Sonnenscheinbewitterungs-Einrichtung für eine Aussetzungszeit von 1.000 Stunden.

2. Ultravioletthärtbare Überzugszusammensetzung gemäß Anspruch 1, worin die Komponente (A) ein mehrwertiges Acrylat enthält mit wenigstens drei Acrylolygruppen im Molekül.

3. Ultravioletthärtbare Überzugszusammensetzung gemäß Anspruch 2, worin die Komponente (A) weiterhin ein polyfunktionelles Acrylat mit zwei Acryloylgruppen im Molekül enthält.

4. Ultravioletthärtbare Überzugszusammensetzung gemäß Anspruch 1, worin die Komponente (D) in einer Menge von 0,5 bis 5 Gew.-Teilen pro 100 Gew.-Teile der Gesamtmenge der Komponenten (A), (B) und (C) vorliegt.

5. Ultravioletthärtbare Überzugszusammensetzung gemäß Anspruch 1, worin die Komponente ausgewählt ist aus Acetophenon und Derivaten davon.

6. Ultravioletthärtbare Überzugszusammensetzung gemäß Anspruch 1, worin die Komponente (E) in einer Menge von 0,5 bis 5 Gew.-Teilen pro 100 Gew.-Teile der Gesamtmenge der Komponenten (A), (B) und (C) vorliegt.

7. Verfahren zur Herstellung einer ultravioletthärtbaren Überzugszusammensetzung gemäß Anspruch 1, umfassend das gleichmäßige Vermischen der Komponenten (A) bis (E) aus Anspruch 1, wobei die Komponente (C) ein Isocyanatäquivalent von 0,4 bis 1,2 pro Hydroxylgruppenäquivalente (B) hat, in einer solchen Menge, daß in dem Endprodukt (A) 30 bis 70 Gew.-% ausmacht, und die Komponenten (B) und (C) 70 bis 30 Gew.-% der Gesamtmenge von (A), (B) und (C) ausmachen.

Revendications

1. Une composition de revêtement durcissable par un rayonnement ultraviolet pour carrosseries de véhicules comprenant :

(A) 30 à 70 % en poids basé sur la quantité totale de (A), (B) et (C) d'un (méth)acrylate polyfonctionnel durcissable par un rayonnement ultraviolet contenant au moins deux groupes (méth)-acryloyles dans la molécule et ayant un poids moléculaire moyen en nombre de 190 à 2 000 ;

(B) un polymère de mono(méth)acrylate d'alcool polyhydrique ayant un indice d'hydroxyle de 10 à 200 choisi parmi les homopolymères de (méth)acrylate d'hydroxyéthyle, de (méth)acrylate d'hydroxypropyle, de mono(méth)acrylate de polyéthylèneglycol, de mono(méth)acrylate de polypropylèneglycol, de mono(méth)acrylate de néopentylglycol et de mono(méth)acrylate de glycérine, ou des copolymères comprenant ces monomères et un ou plusieurs autres monomères copolymérisables, choisis parmi le (méth)acrylate de méthyle, le (méth)acrylate d'éthyle, le (méth)acrylate de propyle, le (méth)acrylate de butyle, le (méth)acrylate de 2-éthylhexyle et le styrène ;

(C) un composé polyisocyanate non-jaunissant ayant un équivalent d'isocyanate de 0,4 à 1,2 par équivalent d'hydroxyle du composant (B) choisi parmi les homopolymères de diisocyanate d'hexaméthylène, les homopolymères de diisocyanate d'isophorone, les copolymères de diisocyanate d'hexaméthylène avec le diisocyanate d'isophorone, les mélanges de ceux-ci et les composés isocyanates bloqués de ceux-ci ; le total de (B) et (C) étant de 70 à 30 % en poids basé sur le total de (A), (B) et (C) ;

(D) un photostabilisant choisi dans le groupe constitué d'un antioxydant du type amine encombrée et d'un absorbant d'ultraviolets du type benzotriazole ; et

(E) un initiateur de photopolymérisation, ladite composition fournissant un film durci ayant une rétention de brillant de 90 % ou plus et une différence de coloration ΔE de 2 ou moins lorsqu'il est testé au moyen d'un appareil weatherometre au soleil pendant un temps d'exposition de 1 000 h.

2. Une composition de revêtement durcissable par un rayonnement ultraviolet selon la revendication 1, selon laquelle le composant (A) contient un acrylate polyfonctionnel ayant au moins trois groupes acryloyles dans sa molécule.

3. Une composition de revêtement durcissable par un rayonnement ultraviolet selon la revendication 2, selon laquelle le composant (A) contient également un acrylate polyfonctionnel ayant deux groupes acryloyles dans sa molécule.

4. Une composition de revêtement durcissable par un rayonnement ultraviolet selon la revendication 1, selon laquelle le composant (D) est présent en quantité de 0,5 à 5 parties en poids pour 100 parties en poids de la quantité totale des composants (A), (B) et (C).

5. Une composition de revêtement durcissable par un rayonnement ultraviolet selon la revendication 1, selon laquelle le composant (E) est choisi parmi l'acétophénone et ses dérivés.

6. Une composition de revêtement durcissable par un rayonnement ultraviolet selon la revendication 1, selon laquelle le composant (E) est présent en quantité de 0,5 à 5 parties en poids pour 100 parties en poids de la quantité totale des composants (A), (B) et (C).

7. Un procédé pour la préparation d'une composition de revêtement durcissable par un rayonnement ultraviolet selon la revendication 1 qui consiste à mélanger uniformément les composants (A) à (E) de la revendication 1, selon laquelle le composant (C) a un équivalent d'isocyanate de 0,4 à 1,2 par équivalent d'hydroxyle du composant (B), en quantité telle que dans le produit final, (A) constitue de 30 à 70 en poids et les composants (B) et (C) constituent de 70 à 30 % en poids de la quantité totale de (A), (B) et (C).